APPLICATION FOR UNITED STATES PATENT

REDUCTION OF NO$_x$ IN LOW CO PARTIAL-BURN OPERATION USING FULL BURN REGENERATOR ADDITIVES

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CROSS-REFERENCE TO RELATED APPLICATION

This application claims benefit of U.S. provisional patent application serial number 60/482,037 filed June 24, 2003.

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CROSS-REFERENCE TO RELATED APPLICATION

[0001]   This application claims benefit of U.S. provisional patent application serial number 60/482,037 filed June 24, 2003.

FIELD OF THE INVENTION

[0002]   The present invention relates to the reduction of the concentrations of nitrogen oxides (NO$_x$) from a fluid catalytic cracking (FCC) regenerator by operating the regenerator in partial CO burn mode with a NO$_x$ reducing catalyst system.

BACKGROUND OF THE INVENTION

[0003]   It has been found that oxides of nitrogen, primarily NO and NO$_2$, are formed at high temperatures, such as the temperature at which catalyst utilized in a hydrocarbon cracking process is regenerated in the presence of carbon monoxide combustion promoters. As hydrocarbons, such as petroleum feedstocks, are cracked, coke is deposited on the catalyst particles. The coke formation on the particles progressively decreases the activity of the catalyst particles. Eventually the activity of the catalyst declines to the point where the coke must be burned off the particles. This step, which is normally referred to as regeneration, may be done on a batch or a continuous basis by contacting the catalyst particles with a hot regeneration gas, such as air. Coke is burned off, thus restoring catalyst activity and simultaneously heating the catalyst. Flue gas formed by burning coke from the catalyst in the regenerator may be treated for

removal of particulates and for conversion of CO to CO_2, after which the flue gas is normally discharged into the atmosphere.

[0004]   Most FCC units now use zeolite-containing catalysts having high activity and selectivity. These catalysts are believed to work best when the amount of coke on the catalyst after regeneration is low. There are two types of FCC regenerators commonly used, the high efficiency regenerator and the bubbling bed type. The high efficiency regenerator mixes recycled regenerated catalyst with spent catalyst, burns much of the coke from the spent catalyst in a fast fluidized bed coke combuster, then discharges the catalyst and flue gas up a dilute phase transport riser where some additional coke combustion occurs, and where most of the CO is afterburned to CO_2. These regenerators are designed for complete CO combustion, and usually produce a relatively coke-free regenerated catalyst, and flue gas with very little CO, and modest amounts of NO_x. The bubbling bed regenerator maintains the catalyst as a bubbling fluidized bed, to which spent catalyst is added and from which regenerated catalyst is removed. These regenerators usually require more catalyst inventory than the high efficiency regenerator does, because gas/catalyst contacting is not as efficient in a bubbling fluidized bed as in a high efficiency regenerator. Many bubbling bed regenerators operate in complete CO combustion mode, i.e., wherein the mole ratio of CO_2/CO is at least 10. Refiners try to burn CO completely within the catalyst regenerator to conserve heat and to minimize air pollution. It is difficult in a catalyst regenerator to completely burn all the coke and convert CO without emitting NO_x with the regenerator flue gas. Increasingly stringent government regulatory emission standards restrict the amount of NO_x that can be present in a flue gas stream discharged to the atmosphere. In

response to environmental concerns, much effort has been spent on finding ways to reduce NO_x emissions.

[0005]   There have been several ways suggested to decrease the amount of NO_x emissions from the regenerator including using a catalyst or additive which is compatible with the FCC reactor, which suppresses NO_x formation or catalyzes its reduction in a regenerator in complete CO burn mode. The inventors herein, however, have unexpectedly discovered that a NO_x reducing catalyst system typically used in complete CO combustion regenerators can provide improved NO_x reduction using a regenerator run in partial burn mode at low CO concentrations.

SUMMARY OF THE INVENTION

[0006]   An embodiment of the present invention provides a process for the catalytic cracking of a nitrogen-containing heavy hydrocarbonaceous feed to lighter products with reduced NO_x emissions, which process comprises:

a) cracking said feed by contacting said feed with a catalyst system in a fluidized catalytic cracking (FCC) reaction zone operating at catalytic cracking conditions to produce a mixture of cracked products and spent cracking catalyst having nitrogen compounds and coke deposited thereon, wherein said catalyst system comprises (i) at least one solid acid component, (ii) at least one metal-containing component comprised of one or more elements from Groups 1 and 3, and one or more elements from Groups 4-15 of the Periodic Table of the Elements; and at least one of oxygen and sulfur, wherein the elements from Groups 1 and 3, Groups 4 – 15 and the at least one of oxygen and sulfur are

chemically bound both within and between the groups and (iii) at least one support, filler, or binder;

b) separating said cracked products from said spent cracking catalyst to produce a cracked product vapor phase stream, which is charged to a fractionation zone, and spent catalyst having nitrogen compounds and carbon deposited thereon, which spent catalyst is charged to a stripping zone;

c) stripping said spent catalyst of volatile compounds in said stripping zone to produce a stripped spent catalyst having coke and nitrogen compounds deposited thereon;

d) regenerating said stripped, spent catalyst with an oxygen-containing gas in a regeneration zone operated at partial CO combustion conditions effective for producing a regenerated catalyst and a flue gas stream containing from about 0.5 to 4 vol. % CO and greater than about 90 ppm by volume, NO, wherein the content of NO_x in said flue gas stream is reduced; and

e) conducting said regenerated catalyst from the regeneration zone to the reaction zone.

[0007] Another embodiment of the present invention provides a process for the catalytic cracking of a nitrogen-containing heavy hydrocarbonaceous feed to lighter products with reduced NO_x emissions, which process comprises:

a) cracking said feed by contacting said feed with a catalyst system in a fluidized catalytic cracking (FCC) reaction zone operating at catalytic cracking conditions to produce a mixture of cracked products and spent cracking catalyst having nitrogen compounds and coke deposited thereon, wherein said catalyst system comprises (i) at least one solid acid component, (ii) at least one metal-containing component comprised of one or more elements from Groups 1 and 3, and one or more elements from Groups 4-15 of the Periodic Table of the

Elements; and at least one of oxygen and sulfur, wherein the elements from Groups 1 and 3, Groups 4 – 15 and the at least one of oxygen and sulfur are chemically bound both within and between the groups and (iii) at least one support, filler, or binder;

b) separating said cracked products from said spent cracking catalyst to produce a cracked product vapor phase stream, which is charged to a fractionation zone, and spent catalyst having nitrogen compounds and carbon deposited thereon, which spent catalyst is charged to a stripping zone;

c) stripping said spent catalyst of volatile compounds in said stripping zone to produce a stripped spent catalyst having coke and nitrogen compounds deposited thereon;

d) regenerating said stripped, spent catalyst with an oxygen-containing gas in a regeneration zone operated at partial CO combustion conditions effective for producing a regenerated catalyst and a flue gas stream containing from about 0.5 to 1 vol. % CO and greater than about 263 ppm by volume, NO, wherein the content of NO_x in said flue gas stream is reduced; and

e) conducting said regenerated catalyst from the regeneration zone to the reaction zone.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0008]   As used herein, the reference to NO_x, or nitrogen oxide(s) refers to the various oxides of nitrogen that may be present in process streams such as, for example, the off-gas of the regenerator of a FCC unit. Thus, the terms refer to all of the various oxides of nitrogen including nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), etc. and mixtures thereof. Of the nitrogen oxides present in the regenerator off-gas, NO typically makes up the majority of

all NO_x present. NO will usually represent about 90% in the regenerator off-gas. Therefore, the presently claimed process is especially concerned with the reduction and control of NO.

[0009]   The present invention provides a FCC process for cracking a nitrogen-containing heavy hydrocarbonaceous feed to lighter products with reduced NO_x emissions. The heavy hydrocarbonaceous feed passes to a FCC process unit which contains at least one reaction zone, a stripping zone, a catalyst regeneration zone, and a product fractionation zone. The feed contacts a NO_x reducing catalyst system in a reaction zone at 425°C-600°C, preferably 460°C-560°C. The hydrocarbons crack, and deposit coke, sulfur, and nitrogen compounds on the catalyst. The cracked products are separated from the coked or spent catalyst. The coked catalyst is stripped of volatiles, usually with steam, in the stripping zone. The stripping is preferably performed under low-severity conditions to minimize thermal cracking. The stripped catalyst is then passed to the regeneration zone where it is regenerated by burning coke on the catalyst in the presence of an oxygen containing gas, preferably air or oxygen-enriched air. This regeneration step restores catalyst activity and simultaneously heats the catalyst to a temperature from about 1202°F (650°C) to about 1382°F (750°C). The environment in the regenerator reduces the amount of coke nitrogen that is converted to reduced nitrogen compounds, such as ammonia, and increases the amount of nitrogen oxides that are produced in the regeneration zone from coke nitrogen. The total amount of oxygen in the regeneration zone is limited so that the regenerator is operated in partial combustion mode.

[0010]   Any conventional FCC feed can be used in the present invention. Such feeds typically include heavy hydrocarbonaceous feeds boiling in the range

of about 430°F to about 1050°F (220°C-565°C), such as gas oils, heavy

hydrocarbon oils comprising materials boiling above 1050°F (565°C); heavy and

reduced petroleum crude oil; petroleum atmospheric distillation bottoms;

petroleum vacuum distillation bottoms; pitch, asphalt, bitumen, other heavy

hydrocarbon residues; tar sand oils; shale oil; liquid products derived from coal

liquefaction processes; and mixtures thereof. Such feeds typically contain an

undesirable amount of nitrogen compounds that are converted to nitrogen oxides

in the regenerator. The FCC feed may also comprise recycled hydrocarbons,

such as light or heavy cycle oils. Preferred feeds in this process are vacuum gas

oils boiling in the range above about 650°F (343°C).

[0011]   The NO_x reducing catalyst system utilized in the present invention

comprises (i) at least one solid acid component, (ii) at least one metal-containing

component comprised of one or more elements from Groups 1 and 3, and one or

more elements from Groups 4-15 of the Periodic Table of the Elements; and at

least one of oxygen and sulfur, wherein the elements from Groups 1 and 3,

Groups 4 – 15 and at least one of oxygen and sulfur are chemically bound both

within and between the groups and (iii) at least one support, filler or binder.

[0012]   The solid acid component is preferably a conventional FCC catalyst

including catalysts containing large-pore zeolites such as USY or REY.

Additional zeolites, which can be employed in accordance with this invention

include both natural and synthetic zeolites. The large-pore zeolites include

gmelinite, chabazite, dachiardite, clinoptilolite, faujasite, heulandite, analcite,

levynite, erionite, sodalite, cancrinite, nepheline, lazurite, scolecite, natrolite,

offretite, mesolite, mordenite, brewsterite, and ferrierite. Included among the

synthetic zeolites are zeolites X, Y, A, L. ZK-4, ZK-5, B, E, F, H, J, M, Q, T, W,

Z, alpha and beta, omega, and USY zeolites. The more preferred large-pore zeolites are the faujasites, particularly zeolite Y, USY, and REY.

[0013] The catalysts useful in the present invention can also be a medium-pore zeolite or a large-pore and medium-pore zeolite mixture. Medium-pore size zeolites that can be used in the practice of the present invention are described in "Atlas of Zeolite Structure Types", eds. W. H. Meier and D. H. Olson, Butterworth-Heineman, Third Edition, 1992, which is hereby incorporated by reference. The medium-pore size zeolites generally have a an average pore diameter less than about 0.7 nm, typically from about 0.5 to about 0.7 nm and includes for example, MFI, MFS, MEL, MTW, EUO, MTT, HEU, FER, and TON structure type zeolites (IUPAC Commission of Zeolite Nomenclature). Non-limiting examples of such medium-pore size zeolites, include ZSM-5, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, silicalite, and silicalite 2. The most preferred is ZSM-5, which is described in U.S. Pat. Nos. 3,702,886 and 3,770,614. ZSM-11 is described in U.S. Pat. No. 3,709,979; ZSM-12 in U.S. Pat. No. 3,832,449; ZSM-21 and ZSM-38 in U.S. Pat. No. 3,948,758; ZSM-23 in U.S. Pat. No. 4,076,842; and ZSM-35 in U.S. Pat. No. 4,016,245. All of the above patents are incorporated herein by reference. Other suitable medium-pore size zeolites include the silicoaluminophosphates (SAPO), such as SAPO-11, SAPO-34, SAPO-41, and SAPO-42, which are described in U.S. Pat. No. 4,440,871; chromosilicates; gallium silicates; iron silicates; aluminum phosphates (ALPO), such as ALPO-11 described in U.S. Pat. No. 4,310,440; titanium aluminosilicates (TASO), such as TASO-45 described in EP-A No. 229,295; boron silicates, described in U.S. Pat. No. 4,254,297; titanium aluminophosphates (TAPO), such as TAPO-11 described in U.S. Pat. No. 4,500,651; and iron aluminosilicates. In one

embodiment of the present invention the Si/Al ratio of said zeolites is greater than about 40.

[0014]   The medium-pore size zeolites can include "crystalline admixtures" which are thought to be the result of faults occurring within the crystal or crystalline area during the synthesis of the zeolites. Examples of crystalline admixtures of ZSM-5 and ZSM-11 are disclosed in U.S. Pat. No. 4,229,424 which is incorporated herein by reference. The crystalline admixtures are themselves medium-pore size zeolites and are not to be confused with physical admixtures of zeolites in which distinct crystals of crystallites of different zeolites are physically present in the same catalyst composite or hydrothermal reaction mixtures.

[0015]   The large-pore and medium-pore catalysts of the present invention will be present in an inorganic oxide matrix component binder that binds the catalyst components together so that the catalyst product is hard enough to survive inter-particle and reactor wall collisions. The inorganic oxide matrix can be made from an inorganic oxide sol or gel which is dried to "glue" the catalyst components together. Preferably, the inorganic oxide matrix is not catalytically active and will be comprised of oxides of silicon and aluminum. It is also preferred that separate alumina phases be incorporated into the inorganic oxide matrix. Species of aluminum oxyhydroxides-γ-alumina, boehmite, diaspore, and transitional aluminas such as α-alumina, β-alumina, γ-alumina, δ-alumina, ϵ-alumina, κ-alumina, and ρ-alumina can be employed. Preferably, the alumina species is an aluminum trihydroxide such as gibbsite, bayerite, nordstrandite, or doyelite. The matrix material may also contain phosphorous or aluminum phosphate. It is within the scope of this invention that the large-pore catalysts

and medium-pore catalysts be present in the same or different catalyst particles, in the aforesaid inorganic oxide matrix.

[0016]   Supported acid materials are either crystalline or amorphous materials, which may or may not themselves be acidic, modified to increase the acid sites on the surface. Non-limiting, illustrative examples are H_2SO_4, H_3PO_4, H_3BO_3, $CH_2(COOH)_2$, mounted on silica, quartz, sand, alumina or diatomaceous earth., as well as heteropoly acids mounted on silica, quartz, sand, alumina or diatomaceous earth. Non-limiting, illustrative examples of crystalline supported acid materials are acid-treated molecular sieves, sulfated zirconia, tungstated zirconia, phosphated zirconia and phosphated nobia.

[0017]   The solid acid component is present with at least one metal-containing component comprised of one or more elements from Groups 1 and 3, and one or more elements from Groups 4-15 of the Periodic Table of the Elements. The remaining component of the catalyst system in accordance with the invention can be at least one of sulfur and oxygen. Oxygen is preferred. The element(s) from Groups 1 and 3 can be any metal or combination of metals selected from lithium, sodium, potassium, rubidium, cesium, francium, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Preferably, the elements from Groups 1 and 3 can be any metal or combination of metals selected from lanthanum and cerium. The element(s) from Groups 4-15 can be any element or a mixture of elements from Groups 4-15 of the Periodic Table of the Elements. Preferably, the element(s) from Groups 4-15 is (are) at least one of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, boron, aluminum, phosphorous, gallium,

germanium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, indium, tin, antimony, hafnium, tungsten, rhenium, iridium, platinum, gold, lead and bismuth. More preferably, the element(s) from Groups 4-15 is (are) at least one of copper, palladium, and silver.

[0018] The catalyst system of the present invention can be prepared by physically mixing or chemically reacting with the metal-containing component and, optionally, combined with the binder to form catalyst particles or act as a filler to moderate the catalyst activity. The weight ratio of solid acid component to the total weight of the metal-containing component can be from about 1000:1 to 1:1000. Preferably, this ratio is about 500:1 to 1:500. Most preferably, this ratio is about 100:1 to 1:100. The weight ratio of the metal-containing component to the matrix component can be about 100:1 to 1:100.

[0019] The metal-containing or NO_x reducing component of the catalyst system may be used as a separate additive particle or as an integral part of a FCC catalyst particle. The NO_x reducing component may contain minor amounts of other materials, which preferably do not adversely affect the NO_x reducing function in a significant way. More preferably, however, the NO_x reducing component consists essentially of items (ii)-(iii) mentioned above. When the NO_x reducing component is used as a separate additive particle, it is added to the inventory of circulating FCC catalyst particles in a NO_x reducing effective amount. An effective amount is an amount, which is effective for reducing the NO_x content in the regenerator flue gas below that which would be present in the absence of the additive. The NO_x reducing component may be combined with at least one support, filler, or binder to form particles suitable for use in a FCC process. If the particle NO_x reduction component is an integral part of a FCC

catalyst particle, it preferably contains from about 0.001 to about 10 percent by weight, and more preferably from about 0.01 to about 5 percent by weight, and most preferably from about 0.05 to about 1 percent by weight of the inventory of circulating particulate solids.

[0020]   While the NO_x reducing catalyst system of the present invention is active for reducing the NO_x content of FCC regenerator flue gas, it has a negligible effect on the hydrocarbon cracking reactions which occur during the FCC process. Furthermore, the NO_x reducing catalyst system is compatible with CO oxidation promoters, which may be part of the inventory of circulating particulate solids. Additionally, the NO_x reducing catalyst system of the present invention may be used with additives that provide SO_x reduction. These SO_x additives may also provide NO_x reduction. The SO_x additives are preferred to be various forms of alumina, rare-earth oxides, alkaline earth oxides, and spinels. More preferably, the SO_x additive is a magnesium-aluminum spinel. SO_x additives are available from several catalyst suppliers, such as Grace-Davison's DESOX or SUPERDESOX, or Intercat's SOXGETTER or Super-SOXGETTER.

[0021]   In a regenerator run under typical partial combustion mode conditions, CO concentrations are generally greater than about 4.0 vol.% with very little NO being present, generally less than about 50 ppm by volume NO. The majority of nitrogen containing species exiting the regenerator at such high CO concentrations are in the form of HCN and NH_3. This is not the optimum use for a NO_x reducing catalyst system. The CO concentration of the present invention, however, is run in partial combustion mode with preferably about 0.5 to about 4.0 vol.% CO, more preferably from about 0.75 to about 3.0 vol.% CO, and most preferably from about 1.00 to about 2.0 vol.% CO. Additionally, NO

concentration is preferably greater than about 90 ppm by volume, more preferably greater than about 150 ppm by volume, and most preferably greater than about 200 ppm by volume. As CO concentration is reduced, more NO is produced, causing more NO reduction with CO, and thereby reducing NO_x emissions. The presence of a circulating NO_x reducing catalyst system increases the rate of NO reduction by CO, thereby causing additional reduction in NO_x emissions.

[0022] The hot regenerated catalyst is recycled to the FCC reaction zone where it contacts injected FCC feed.

[0023] The reactor operation will usually be conventional all riser cracking FCC, such as disclosed in U.S. Pat. No. 4,421,636 incorporated herein by reference. Typical riser cracking reaction conditions include catalyst/oil ratios of 0.5:1 to 15:1, preferably 3:1 to 8:1, and a catalyst contact time of 0.1-50 seconds, preferably 0.5 to 10 seconds, most preferably about 0.75 to 5 seconds, and riser top temperatures of 900°F to about 1100°F, preferably 950°F to 1050°F.

[0024] It is preferred to have good mixing of feed with catalyst in the base of the riser reactor, using conventional techniques such as adding large amounts of atomizing steam, use of multiple nozzles, use of atomizing nozzles and similar technology. The Atomax nozzle, available from the M. W. Kellogg CO, is preferred. Details of a suitable nozzle are disclosed in U.S. Pat. Nos. 5,289,976 and 5,306,418, which are incorporated herein by reference. It is preferred, but not essential, to have a riser catalyst acceleration zone in the base of the riser. It is also preferred, but not essential, for the riser reactor to discharge into a closed cyclone system for rapid separation of cracked products from spent catalyst. A

closed cyclone system is disclosed in U.S. Pat. No. 4,502,947 to Haddad et al., which is incorporated herein by reference. It is also preferred but not essential, to rapidly strip the catalyst as it exits the riser upstream of the catalyst stripper. Stripper cyclones disclosed in U.S. Pat. No. 4,173,527, Schatz and Heffley, incorporated herein by reference, may be used. It is preferred, but not essential, to use a hot catalyst stripper. Hot strippers heat spent catalyst by adding hot, regenerated catalyst to spent catalyst. A hot stripper is shown in U.S. Pat. No. 3,821,103, Owen et al, incorporated herein by reference. After hot stripping, a catalyst cooler may cool heated catalyst before it is sent to the regenerator. A preferred hot stripper and catalyst cooler is shown in U.S. Pat. No. 4,820,404, Owen, incorporated herein by reference. Conventional FCC steam stripping conditions can be used, with the spent catalyst having essentially the same temperature as the riser outlet, and with 0.5 to 5% stripping gas, preferably steam, added to strip spent catalyst. The FCC reactor and stripper conditions, per se, can be conventional.

[0025]   Two types of FCC regenerators can be used in the process of the present invention, the high efficiency regenerator and the bubbling bed type. In bubbling bed regenerators, much of the regeneration gas, usually air, passes through the bed in the form of bubbles. These pass through the bed, but contact it poorly. These units operate with large amounts of catalyst. The bubbling bed regenerators are not very efficient at burning coke so a large catalyst inventory and long residence time in the regenerator are needed to produce clean burned catalyst. The carbon levels on regenerated catalyst can be conventional, typically less than 0.3 wt % coke, preferably less than 0.15 wt % coke, and most preferably even less. By coke we mean not only carbon, but also minor amounts of hydrogen associated with the coke, and perhaps even very minor amounts of

unstripped heavy hydrocarbons which remain on catalyst. Expressed as wt % carbon, the numbers are essentially the same, but 5 to 10% less.

[0026]   There should be enough CO present in the flue gas so that the FCC regenerator can be reliably controlled using control techniques associated with partial CO combustion.

[0027]   The process or the present invention can also be used with high efficiency regenerators (HER), with a fast fluidized bed coke combustor, dilute phase transport riser, and second bed to collect regenerated catalyst. It will be necessary to operate these in partial CO burn mode to make CO specifications.

[0028]   HERs inherently make excellent use of regeneration air. Most operate with 1 or 2 mole % O_2 or more in the flue gas when in complete CO burn mode. When in partial CO burn mode most operate with little excess oxygen, usually in the ppm range, preferably less than 1/10th %. For HER's, significant reductions in the amount of air added may be necessary to produce a flue gas with the correct CO/O_2 ratio. Reducing or eliminating CO combustion promoter may be necessary to generate a flue gas with twice as much CO as oxygen.

[0029]   Although most regenerators are controlled primarily by adjusting the amount of regeneration air added, other equivalent control schemes are available which keep the air constant and change some other condition. Constant air rate, with changes in feed rate changing the coke yield, is an acceptable way to modify regenerator operation. Constant air, with variable feed preheat, or variable regenerator air preheat, are also acceptable. Finally, catalyst coolers can be used to remove heat from a unit. If a unit is not generating enough coke to

stay in heat balance, torch oil, or some other fuel may be burned in the regenerator.

EXAMPLE 1:

[0030]   The present invention was tested and developed using a commercial FCC process unit. In the experiment, CO concentration in the flue gas at the outlet of the FCC unit regenerator was varied from above approximately 0.5 vol.% to approximately 5.5 vol.%. Over that range of CO concentration, NO concentration varied from a maximum of about 266 ppm by volume down to a minimum of approximately 31 ppm by volume (Table 1). The accepted reaction mechanism for minimizing NO_x emissions from the FCC unit regenerator requires operation in a regime where significant concentrations of both NO and CO exist.

[0031]   In partial-burn operations, at very high CO concentrations there is little NO available (nitrogen species are primarily NH3 and HCN) for reduction with CO. Moreover, relatively high NO_x emissions are found. As CO concentration was reduced, more NO was produced, causing more NO reduction with CO, and thereby reducing NO_x emissions. Below about 1% CO, the NO concentration asymptoted to a constant, maximum value, and NO_x emissions were at the lowest value. See Table 1 and Figure 1.

[0032]   The region of very low CO concentration simulates CO and NO concentrations that may be found in a full CO burn operation at low excess O_2. For such full-burn units, NO_x reducing catalyst systems have proven to be effective. In partial-burn units, where the CO concentration is typically above 4

vol.%, these NO_x reducing catalyst systems are relatively ineffective. This invention recognizes that at very low CO operation, the NO_x reducing catalyst system is much more effective than in typical partial-burn operation because the key species (NO and CO) both exist in significant concentrations.

TABLE 1

NO concentrations are at a maximum at low CO concentrations.	
CO (Vol.%)	**NO (vppm)**
0.50	266
0.75	266
1.00	263
1.25	257
1.50	248
1.75	237
2.00	223
2.25	209
2.50	193
2.75	176
3.00	158
3.25	141
3.50	123
3.75	106
4.00	90
4.25	75
4.50	62
4.75	50
5.00	41
5.25	35
5.50	32
5.75	31